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Supercritical Fluid Extraction with Simultaneous Class Fractionation of PCBs and PAHs from Adsorbent Materials for Air Pollution Determinations

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Introduction

The Soxhlet leaching of adsorbent materials containing trapped organics, has traditionally been used for sample preparation for determination of trace contaminants in ambient air. This liquid extraction procedure is time consuming and create large amount of organic solvent waste. In the past few years, supercritical fluid extractions have shown excellent characteristics for rapid extraction of the organic contaminants from different matrices. In this paper, Supercritical Fluid Extraction (SFE) has been developed as an alternative to Soxhlet extraction for the determination of the trace organic contaminants in ambient air. In addition, PCBs and PAHs can be simply class fractionated when Florisil™ is used as a sorbent and by varying SFE conditions.

Experimental

The following materials were used for adsorbents in the extraction studies: Florisil™, 60/100 mesh, C18, XAD, Tenax™, Silica gel and Polyurethane Foam (PUF). Each adsorbent was cleaned by the Soxhlet method of extraction, with 250 ml of hexane for 20 hours. A standard hexane mixture was prepared containing selected PAHs and PCBs which are Acenaphthylene(ACE), 2,2',5-Trichlorobiphenyl(PCB3), 2,2',3,4,5-Pentachlorobiphenyl(PCB5), Benzo(a)anthracene(BEN), 2,2',3,4,4',5,6,6'-Octachlorobiphenyl(PCB8), Decachlorobiphenyl(PCB10), Indeno(1,2,3-cd)pyrene(IND), Coronene(COR), Benzo(g,h,i)perylene(BEP), and 2-Methyl-anthracene(Internal Standard).

SFE was performed with a high-pressure vessel which was constructed of stainless steel in the Science Machine Shop at the University of Waterloo. The vessel with a volume of 200 ml could withstand pressure in excess of 20000 psi. At the outlet of the pressure vessel, an extraction vessel consisted of two 1/4" to 1/16" reducing unions, 316 stainless steel fittings (Swagelok) and a 2.25" SS tubing. A 20 cm x 25 µm fused silica capillary was connected to the extraction vessel acting as a restrictor to maintain the pressure in the system. The capillary was directed into a 1.8-ml vial containing approximately 1.0 ml of hexane. The supercritical fluid sample was collected in the vial and concentrated to 100 µl with a gentle stream of nitrogen.

Three procedures were performed in the experiments. The first procedure was to determine which adsorbent would be the best to enable quantitative recoveries of all selected PCBs and PAHs from the matrices. Each adsorbent was spiked by injecting a small volume (100 µl) of standard mixture solution. The adsorbent in the vessel was then extracted with N₂O or N₂O with 6.5% by volume of modifier at 6000 psi for 30 minutes. The second procedure was to test the adsorbents' (XAD, Tenax™, Florisil™) ability to effectively contain trace organic contaminants during the adsorption and drying steps of the analytical process by spiking 100 µl of the standard mixture directly on top of the selected adsorbent in the extraction vessel, and passing moisture through the adsorbent for 24 h. Then the moisture was removed from the adsorbent by purging dry nitrogen through the extraction vessel for 30 minutes at 60°C. The saturated and dried adsorbent containing standard mixture was then extracted using N₂O with 6.5% by volume of modifier at 6000 psi for 30 minutes. The third procedure was to fractionate PCBs from PAHs by varying pressure of supercritical fluid N₂O.

A Varian 3500 capillary gas chromatograph, equipped with a splitless injector, a flame ionization detector (FID), and a 30 m x 0.25 µm fused silica capillary column (DB-5, J & W Scientific, California) was used for chromatographic analysis. The oven temperature was programmed to ramp from 140°C to 225°C at 15°/min, then to 300°C at 20°C/min and held there for 14 minutes. The FID temperature was set at 325°C. The temperature of the injector was set at 300°C.

Results and Discussion

Six commercially available adsorbents are evaluated for their ability of recovering contaminants. As shown in Table 1, all PCBs could be extracted quantitatively with pure N₂O. However, PAH compounds, particularly IND and COR were poorly recovered because of strong interaction of these large compounds with the matrix.

Table 2 shows the percentage recoveries of the standard mixture from the selected adsorbents using supercritical N₂O plus 6.5% by volume (100 µl) of methanol modifier. This method quantitatively recovered all compounds in the standard mixture from PUF, Florisil™, C18, Silica Gel, and Tenax™. The difficulties in recovering high molecular weight PAHs from XAD still remain. Table 3 shows the percentage recoveries of the standard mixture from the selected adsorbents using supercritical N₂O plus 6.5% by volume of toluene modifier. Similar to Table 2, this method can also improve the recoveries of IND and COR but in a lesser extent than using methanol modifier. Quantitative recoveries of all compounds from XAD are obtainable with this conditions. This may indicate that the energy barrier of desorption between the analyte and adsorbent can be reduced by selective interaction of aromatic ring in toluene with the matrix-solute complex since XAD resins also contain aromatic rings in their structure. For other adsorbents, the method involved toluene modifier results in lower recoveries.

Apparently, if XAD is chosen to be the adsorbent, the method using toluene modifier will be superior than other modifier while methanol is suitable for the other five adsorbents. In air sampling, the trace organic contaminants along with moisture from the air are trapped in the adsorbent matrices contained in a cartridge. The moisture must be removed from the adsorbent to ensure successful SFE and gas chromatographic analysis. Three adsorbents (XAD, Tenax™, Florisil™) were investigated by comparing their

Table 1. The average recoveries for the extractions with pure N₂O at 6000 psi and 40°C

Compound	XAD	PUF	Florisil™	C ₁₈	Silica Gel	Tenax
ACE	111.3 ± 3	94.2 ± 1	78.4 ± 6	84.1 ± 6	64.3 ± 1	87.1 ± 4
PCB3	105.0 ± 3	98.5 ± 1	99.0 ± 10	94.6 ± 5	88.0 ± 2	93.9 ± 1
PCB5	94.8 ± 5	91.9 ± 3	89.2 ± 1	95.2 ± 3	94.3 ± 1	97.0 ± 1
BEN	96.8 ± 2	90.5 ± 1	71.1 ± 6	93.1 ± 2	102.5 ± 2	99.1 ± 2
PCB8	91.6 ± 9	92.1 ± 1	76.9 ± 3	84.6 ± 4	100.5 ± 3	97.0 ± 2
PC10	89.3 ± 12	92.3 ± 1	71.0 ± 8	71.7 ± 15	101.9 ± 2	97.0 ± 2
IND	76.4 ± 13	83.0 ± 3	45.0 ± 5	75.7 ± 14	88.8 ± 9	84.0 ± 2
COR	12.0 ± 8	53.3 ± 4	2.2 ± 1	46.2 ± 15	35.5 ± 4	54.7 ± 4

Table 2. The average recoveries for the extractions with N₂O + methanol at 6000 psi and 40°C

Compound	XAD	PUF	Florisil™	C ₁₈	Silica Gel	Tenax
ACE	109.1 ± 13	92.3 ± 2	86.7 ± 3	80.0 ± 2	112.8 ± 19	84.4 ± 1
PCB3	127.2 ± 17	118.5 ± 10	95.4 ± 3	97.8 ± 2	146.3 ± 15	93.2 ± 0.2
PCB5	102.4 ± 6	119.8 ± 3	91.1 ± 2	98.7 ± 4	126.9 ± 8	103.9 ± 2
BEN	64.8 ± 19	96.8 ± 4	139.0 ± 2	97.9 ± 7	135.2 ± 4	106.3 ± 0.3
PCB8	91.6 ± 11	113.1 ± 0	92.6 ± 1	99.0 ± 6	97.7 ± 14	102.2 ± 0.4
PC10	91.7 ± 14	109.8 ± 2	90.1 ± 1	99.1 ± 7	111.3 ± 2	101.9 ± 0.2
IND	65.4 ± 1	100.3 ± 11	92.6 ± 1	100.3 ± 13	157.5 ± 15	92.3 ± 1
COR	50.1 ± 2	83.6 ± 13	89.8 ± 10	106.5 ± 13	97.7 ± 11	81.8 ± 2

Table 3. The average recoveries for the extractions with N₂O + toluene at 6000 psi and 40°C

Compound	XAD	PUF	Florisil™	C ₁₈	Silica Gel	Tenax
ACE	87.3 ± 4	64.0 ± 1	74.0 ± 11	62.5 ± 23	62.3 ± 1	72.1 ± 2
PCB3	104.8 ± 9	93.3 ± 4	92.3 ± 10	78.6 ± 10	78.9 ± 1	90.8 ± 4
PCB5	94.8 ± 7	91.5 ± 2	80.6 ± 9	71.3 ± 2	73.9 ± 5	84.9 ± 4
BEN	96.3 ± 8	85.4 ± 37	97.0 ± 14	74.4 ± 3	75.0 ± 1	96.4 ± 8
PCB8	101.4 ± 11	79.3 ± 3	76.5 ± 8	70.1 ± 2	75.5 ± 5	85.3 ± 3
PC10	107.8 ± 14	78.6 ± 5	80.8 ± 9	73.6 ± 2	78.7 ± 5	91.1 ± 2
IND	99.8 ± 5	45.9 ± 9	81.2 ± 29	88.8 ± 4	82.6 ± 3	94.2 ± 2
COR	84.6 ± 2	68.7 ± 4	4.6 ± 1	81.5 ± 1	77.6 ± 10	76.3 ± 9

abilities to contain trace organic contaminants during adsorption, and retain those contaminants during the drying step.

Table 4 shows the average recoveries of components from saturated with moisture and then dried adsorbents. The following observations are made: the percentage recoveries for PCBs are generally good, being independent of the nature of adsorbents; the percentage recoveries for PAHs from XAD and Florisil™ are low compared to those obtained from previous experiments (the spiked standard mixture could be extracted quantitatively using N₂O with 100 µl of modifier at 6,000 psi and 40°C). There is no significant loss of analytes during the adsorbing and drying processes when Tenax™ is used as an adsorbent.

Table 5 shows the quantitative recoveries of target contaminants are obtained when the amount of toluene or methanol is increased from 100 µl to 150 µl or 200 µl (200 µl of toluene to XAD and 150 µl of methanol to Florisil™). This method significantly improves the recoveries of IND and BEP from the saturated, dried XAD or Florisil™.

It has been found that aging of XAD spiked with 100 µl standard mixture for 24 hours at room temperature lowers the percentage recoveries of all PAHs except acenaphthylene. Table 6 shows the comparison of percentage recoveries from aged XAD with the percentage recoveries from spiked XAD (Extractions were immediately done after a standard mixture was spiked onto the adsorbent). Spiked PAHs can be extracted quantitatively from XAD using N₂O with 100 µl of toluene since thermal energy easily overcomes the low energy barriers associated with weekly adsorption between the spiked PAHs and the matrix.

In the case of saturated then dried PAHs, because of the aging of PAHs for 24 hours during saturating process, the desorption is more difficult, the PAHs become strongly adsorbed onto active sites of the adsorbent. In order to extract strongly adsorbed analytes which bond to sites of XAD or Florisil™, the

Table 4. The average recoveries of contaminants from saturated and dried adsorbents

Conditions SF: N ₂ O 6,000 psi 40°C 30 min	ACE	PCB3	PCB5	BEN	PCB8	PCB10	IND	BEP
Sat., dried XAD 100 µl of Toluene	85.2 ± 9.9	92.5 ± 4.9	101.2 ± 3.5	65.8 ± 20.8	109.0 ± 2.7	109.1 ± 3.4	8.9 ± 4.7	7.7 ± 2.4
Sat., dried Tenax 100 µl of MeOH	93.0 ± 0.4	97.3 ± 4.3	101.2 ± 5.5	80.5 ± 3.8	101.7 ± 2.4	98.4 ± 3.2	89.2 ± 9.4	84.0 ± 4.3
Sat., dried Florisil 100 µl of MeOH	68.7 ± 2.7	84.1 ± 0.6	89.4 ± 4.4	79.8 ± 2.0	85.5 ± 5.6	83.9 ± 9.8	72.2 ± 13.1	68.2 ± 13.6

Table 5. The percentage recoveries of contaminants from saturated and dried adsorbents using a large amount of modifier

Conditions SF: N ₂ O 6,000 psi 40°C 30 min	ACE	PCB3	PCB5	BEN	PCB8	PCB10	IND	BEP
Sat., dried XAD 200 µl of Toluene	87.2 ± 4.5	96.3 ± 5.2	104.1 ± 7.2	108.8 ± 8	108.5 ± 9.4	101.8 ± 6.9	96.3 ± 7.7	86.2 ± 5.7
Sat., dried Florisil 150 µl of MeOH	71.3 ± 3.5	90.4 ± 2.7	94.3 ± 4.4	78.9 ± 6.9	108.9 ± 33.6	87.9 ± 4.4	83.6 ± 8.1	82.8 ± 6.6

Table 6. Comparison of percentage recoveries from aged XAD with spiked XAD

CONDITIONS	ACE	PCB3	PCB5	BEN	PCB8	PCB10	IND	BEP or COR
Aged XAD for 24 h 100 µl of STD N ₂ O+100 µl of Toluene 6,000 psi 30 min 40°C	89.4 ± 16.2	106.1 ± 14.8	109.1 ± 13.4	58.6 ± 12.1	103.3 ± 10.7	98.5 ± 12.9	19.0 ± 4.1	16.5 ± 4.3
Spiked XAD 100 µl of STD N ₂ O+100 µl of Toluene 6,000 psi 30 min 40°C	87.3 ± 4.0	104.8 ± 9.0	94.8 ± 7.0	96.3 ± 8.0	101.4 ± 11.0	107.8 ± 14.0	99.8 ± 5.0	84.6 ± 2.0

Table 7. Fractionation of PCBs from PAHs with Florisil™

Conditions	ACE	PCB3	PCB5	BEN	PCB8	PCB10	IND	BEP
N ₂ O 2,000 psi 25 Min 40°C	83.7 ± 1.3	92.0 ± 2.2	95.0 ± 6.7	0	119.1 ± 10.2	89.6 ± 6.0	0	0
N ₂ O/MeOH 6,000 psi 30 min 40°C	2.2 ± 2.2	2.6 ± 2.6	10.6 ± 10.6	78.6 ± 15.2	0	0	73.8 ± 2.8	77.6 ± 0.6

amount of solvent to break the specific interaction between the target analyte and sorptive sites on the adsorbent, such as XAD, Florisil™, must be increased.

Five adsorbents were investigated to determine which would be the best adsorbent for fractionating PAHs from PCBs. The method can simplify the analysis of the complex mixtures and possibly remove the interferences from adsorbent in the air pollution studies. Results obtained from XAD, Tenax™, C18, and Alumina show that these adsorbents cannot be used to fractionate PCBs from PAHs by varying pressure using N₂O or CO₂ since there is a large overlap between both groups. The Florisil™ is the best adsorbent providing fractionation of PCBs from PAHs. Quantitative recoveries of the PCBs were obtained from Florisil™ at 2,000 psi while 70 percentage recoveries of PAHs except ACE were extracted at 6,000 psi with modified N₂O (Table 7).

This becomes evident when examining extraction pressure variation studies (Figure 1). The PCBs are quantitatively extracted with N₂O at 2,000 psi from Florisil™. BEN is partly extracted at 3,000 psi but it is not quantitatively recovered until the pressure of the N₂O is increased to 6,000 psi. IND and BEP are quantitatively recovered only at 6,000 psi with modified N₂O. These results tend to indicate that the fractionation of the analytes from Florisil™ is based on the classes of compounds rather than on molecular weight. For example, PCB10 has a higher molecular weight (499) than indeno (1,2,3-cd) pyrene (276), and PCB10 is extracted at 2,000 psi with other PCBs rather than PAHs. The ACE is also removed with PCBs at 2,000 psi possibly due to its lower molecular weight and boiling point.

Currently our efforts are focused on replacing nitrous oxide with carbon dioxide when modifiers are used. Initial results indicate that similar recoveries are obtained, but the extraction times are increased by about 50 %.

Conclusions

Polychlorinated biphenyls and polycyclic aromatic hydrocarbons can be quantitatively recovered from adsorbents such as XAD resin, PUF, Florisil™ and Tenax™ with SFE. SFE with methanol or toluene will result in higher percent recoveries than the extractions without modifier.

During the adsorbing and drying steps of the analytical process, no significant loss of compounds contained on all adsorbents is found. However, an aging effect was observed, which requires the addition of larger amounts of modifier to obtain full recoveries.

Fractionation of PCBs from PAHs can be performed from Florisil™ using N₂O with MeOH as a modifier by varying the extraction condition.

SFE is an better alternative to Soxhlet extraction for the determination of trace organic contaminants in the ambient air, which significantly simplifies analyses and shortens extraction time by about an order of magnitude.

Figure 1. The percent recoveries obtained by varying the pressure of the supercritical N₂O

